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PHOTOACOUSTIC SPECTROSCOPY*

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SPECTROSCOPY, Photoacoustic

During the past year, there have been several important advances in photoacoustic spectroscopy; advances that have further extended the capabilities of this new methodology.

Analytical Applications

Photoacoustic spectroscopy is now routinely used to study all three phases of matter -- gases, liquids and solids. For gaseous samples and for most solid samples, a photoacoustic spectrometer with a gas-microphone mode of detection is usually used. Liquids can also be studied with such an apparatus, although the signal strength is considerably reduced for liquids with low optical absorptions. Recently, however, several researchers have performed photoacoustic studies on liquids by means of a piezoelectric mode of detection. In these experiments, the liquid sample completely fills a small chamber that is itself made of piezoelectric material, and the photoacoustically generated heat pulses within the liquid are detected as stress-strain signals by the piezoelectric chamber. With this method, all of the optical energy observed by the sample, that decays non-radiatively, can contribute to the photoacoustic signal, whereas in the gas-microphone method only that energy absorbed within a thermal diffusion length of the sample-gas boundary can contribute to the signal.

The piezoelectric cell is thus better suited to the measurement of very small optical absorptions in liquid samples. Using such a method, researchers have been able, recently, to detect minute traces of metal ions in solution (0.02 ng/ml). This value is almost two orders of magnitude lower than that obtained from calorimeter analysis or from flame absorption measurements.

Catalytic and Surface Studies

One of the major advantages of photoacoustic spectroscopy lies in its relative immunity to scattered light, and its subsequent ability to provide absorption spectra of highly light-scattering materials such as powders. This capability is being put to good use in the study of catalytic compounds and catalytic reactions. For example, several recent studies of this nature, involve the reactions of transition metal complexes with polymeric ligands to form anchored catalysts. Photoacoustic spectroscopy has been used very effectively to investigate the electronic structures of these metal-polymer complexes in order to elucidate chemical processes and structure-reactivity relationships.

The ability of photoacoustics to detect absorption processes in the presence of strong light scattering and reflection has also made the technique useful in surface studies. Photoacoustic surface studies have been performed previously in the visible region, but more useful data can be obtained in the mid-infrared since the molecular information there is more detailed and specific. Unfortunately, widely tunable infrared light sources are not available with sufficient intensity for a conventional photoacoustic spectrometer. Work is progressing at several laboratories to develop Fourier-transform photoacoustic spectrometers that will operate in the mid-infrared region. In the meantime, P.-E. Nordal and S. Kanstad have demonstrated the power of the photoacoustic method for infrared surface studies. Using a CO_2 laser, they demonstrated that it is possible to measure absorptions on surface layers that are only Angstroms thick. This is a sensitivity comparable to that attainable with electron energy loss spectroscopy, but with the advantage of optical spectral resolution.

Deexcitation

The photoacoustic effect measures the heat-producing deexcitation processes that occur in a system after it has been optically excited. This selective sensitivity of photoacoustics to the heat-producing deexcitation channel has been used to great advantage in the study of fluorescent materials, and in the study of photosensitive materials that exhibit photochemistry or photoconductivity.

These capabilities have been amply illustrated by recent experiments of D. Cahen and his co-workers. In one set of experiments, they studied the mechanism of photosynthesis both in green plant matter and in bacteria. They were able to obtain the activation spectrum for photosynthesis, and to study the role of inhibitors, and the effects of intermediate storage states. In another experiment, D. Cahen used photoacoustics to investigate the photovoltaic process in silicon, and demonstrate how photoacoustics could be used to measure the photovoltaic efficiency of candidate materials for solar cells.

Phase Transitions

The photoacoustic signal depends not only on the optical properties of the sample, but also on its thermal properties. Since these thermal properties generally undergo a change when the material undergoes a phase transition, monitoring the photoacoustic signal as a function of temperature can provide information about these phase transitions. This application of photoacoustics was recently demonstrated by R. Florian and his co-workers. Using photoacoustics, they investigated the first-order liquid-solid transitions of gallium and of water, and the first-order structural phase transition of K_2SnCl_6. They found that not only do the magnitude and phase of the photoacoustic signal change when the thermal parameters of the sample change, but that, in addition, a strong modification in both amplitude and phase signals occurs when a first-order transition is approached from lower temperatures. This is a result of the fact that during the endothermic cycle of the phase transition, the periodic heat generated by the photoacoustic process is itself absorbed by the endothermic event, and is therefore lost, resulting in large changes in both the amplitude and phase of the photoacoustic signal. The application of photoacoustics to phase transition studies should constitute a useful complementary technique to the conventional calorimeter methodology.

Bibliography

A. Rosencwaig, Adv. Electronics and Electron Physics, vol. 46, 208, Academic Press, New York, 1978; P.-E. Nordal and S. O. Kanstad, Opt. Commun. 24, 95 (1978); D. Cahen, S. Malkin and E. I. Lerner, FEBS Lett. 339 (1978). R. Florian, J. Pelzl, M. Rosenberg, H. Vargas and R. Wernhardt, Phys. Stat. Sol., 48, K35 (1978).